

Full Paper

## A Polymeric Membrane Electrode Based on *p*-tert-butyl-thiacalix[4]arene Derivative for Thorium Determination

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**Abstract-** The aim of this study was to construct and characterize an ion selective electrode for the potentiometric determination of thorium ions. On hand study we introduced a new calixarene molecule *p*-tert-butyl-thiacalix[4]arene derivative as ionophore for thorium(IV) selective polymeric membrane electrode. Due to the decisive role of solvent mediators, we fabricated membranes with the plasticizers DBP, DBBP, TEP, OA, DOP, 1-CN respectively and anionic additive NaTPB. The best of the results were obtained with the membrane electrode composition of DBP:PVC:Ionophore:NaTPB (57%:35%:6%:2%). Electrode sensor shows excellent discrimination towards Th<sup>4+</sup> ion in presence of other common cations. The resulting data clarified that the electrode shows a Nernstian slope of 14.9±0.6 mV per decade for Th(IV) ions over a broad working concentration range of 8.0×10<sup>-8</sup> to 1.0×10<sup>-1</sup> mol/L. Our electrode gives the potential response in 7 sec for whole concentration range and this sensor can be used for seven months. Electrode has been successfully applied for many environmental and biological samples of thorium (IV) and as an indicator in potentiometric titration.

**Keywords-** Thorium Selective Electrode, *p*-tert-butyl-thiacalix[4]arene Derivative, Polymeric Membrane.

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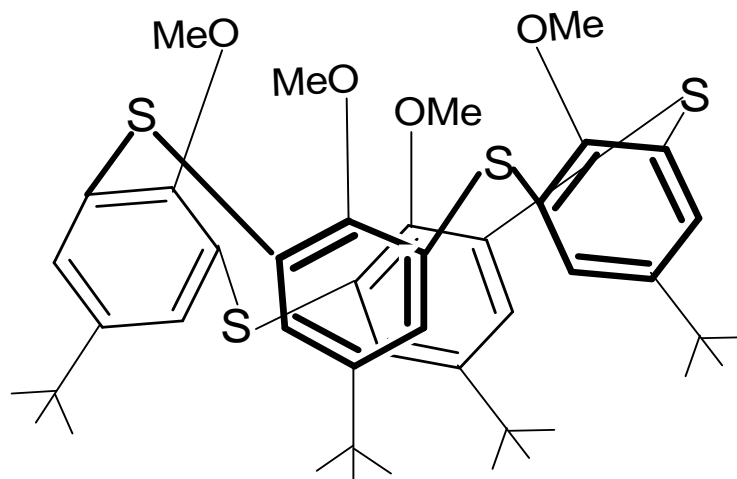
## 1. INTRODUCTION

Thorium is a radioactive substance and occurs naturally in low concentrations in the earth's crust. It is used as a fuel for nuclear reactor in place of uranium because thorium is three times more abundant than uranium. Thorium is very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant), of ingestion, of inhalation. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Prolonged exposure to the substance can produce target organs damage. Since thorium has the ability to change genetic arrangements, it may increase the chances of developing the lung diseases and pancreas cancer [1,2,3]. Since thorium is found almost everywhere, you will be exposed to small amounts of it in the air you breathe and in the food and water you eat and drink. You can come into contact with it in the environment through breathing air, eating, drinking, or smoking substances containing the radioactive chemical. Exposure may also result from skin contact with the radioactive chemical alone, or with a substance containing it. Exposure can also occur by being near radioactive chemicals in concentrations that may be found at hazardous waste sites or at industrial accidents.

Conventional methods available for precise and accurate determination of actinides metal ions are Activation analysis, inductively coupled Plasma- Mass Spectroscopy (ICP-MS), ICP-AES and Isotope dilution mass spectroscopy. These are elaborate, time consuming methods and involve sophisticated equipment that might not be available in most analytical labs. The increase use of ion sensors in the field of environmental, agricultural, industrial, medical and pharmaceutical analysis is simulating analytical chemists to develop new sensors for fast, accurate, reproducible and selective determination of various ions [4]. Potentiometric sensor offers an inexpensive and convenient method for analysis of heavy metal ions in solutions with acceptable sensitivity and selectivity.

The wide range of ion selective electrodes (ISE) may be extended by the use of membranes of some new polymers. The development of a good sensitive sensor for thorium ion has long been a subject of concern to analytical chemists but still not much effort has been made in this direction in the last four decades. However there are four electrodes reported in the literature based on the following ionophores such as thorium 8-hydroxyquinolate [5], tin(IV) tungstoselenate-pyridine [6], 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy)calix[4]arene [7], 2,3,7,8-tetraphenyl-1,4,6,9-tetraaza-cyclodeca-5,10-dithion-1,3,6,8-tetraene [8]. But these potentiometric thorium sensors suffer from such disadvantage as high detection limits, short linear ranges, high response time and significant interferences from many cations.

In our research paper, we are introducing a highly selective and sensitive thorium (IV) sensor based on a new thiacalix[4]arene compound as an excellent ion carrier for the selective determination of thorium(IV) ions.



**Fig. 1.** Structure of ionophore *p*-*tert*-butyl-thiacalix[4]arene derivative

## 2. EXPERIMENTAL

### 2.1. Reagents

All the analytical grade reagents were used as purchased. High molecular weight poly(vinyl chloride) (PVC), 1-chloronaphthalene (CN), oleic acid (OA), dibutyl-butylphosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), tris(2-ethylhexyl)phosphate (TEP), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF), cyclohexanone were purchased from Merck. All metal nitrates were also brought from Merck. Doubly distilled deionized water was used throughout. Stock solution of metal nitrates of  $10^{-1}$  M concentration was obtained by dissolving weighed amounts of corresponding salt in double distilled water. Solutions of  $10^{-2}$ - $10^{-8}$  M concentration were obtained by diluting stock solution.

### 2.2. Instrument

Absorption spectra were measured by  $\lambda=35$  UV/Vis Spectrophotometer and saturated calomel electrodes (SCE) were used as reference electrodes; a digital potentiometer ECIL, India (Model pH 5662) is used for potential measurements at  $25 \pm 0.1$  °C.

**Ionophore Synthesis [9]:** A mixture of *p*-*tert*-butylphenol (64.5 g, 0.43 mol) and elemental sulphur S8 (27.5 g, 0.86 mol), and NaOH (8.86 g, 0.215 mol) were mixed in tetraethylene glycol dimethyl ether (19 ml). The mixture was heated gradually to 230 °C over a period of 3-4 h and maintained at this temperature for a further 3 h with simultaneously removal of H<sub>2</sub>S with a slow stream of nitrogen. Dark red colored product was cooled to ambient temperature and washed with toluene and then with ether. After that 0.5 M aq. sulfuric acid solution was added with stirring to give a suspension. By filtration precipitate was collected and then did methylation

at phenolic oxygen. Finally product was recrystallized from chloroform and dried in vacuum oven (100 °C) for 4 h.

### 2.3. Electrode construction

To fabricate the polymeric membrane we used dipping method [10] and a mixture of 35% PVC, 57% plasticizer (DBBP, DBP, TEP, 1-CN, OA, DOP respectively), 2% NaTPB, and 6% ionophore dissolved in THF. Mixture was shaken vigorously to obtain homogenous phase and after complete dissolution of all components it was poured in to the glass cast ring placed on a smooth glass plate and kept for 48 h for solvent evaporation. After this a membrane with uniform thickness was obtained. The membrane of 0.5 mm thickness were removed carefully from the glass cast ring and cut it to the size of the Pyrex glass tube and glued it to one end of a glass tube with the help of araldite and M-seal to avoid leakage.

Potential measurement: Emf measurements were carried out with the cell assembly given below:

Internal reference electrode (SCE)	Internal reference solution (0.01 M Th <sup>4+</sup> )	Thorium Selective Membrane	Test solution	External reference electrode (SCE)
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Two half cells were combined with the help of salt bridge. The potential measurements were made from low to high concentration range to avoid the memory effect. After each dilution pH was checked and adjusted with diluted HNO<sub>3</sub>/hexamine to the value from the range 2.0-9.0. Response time of each membrane sensor, i.e. the time needed for stable and constant potential readings, was determined by measuring electrode potentials at different times.

Electrode conditioning: The ionic strength of various solutions was maintained with the help of saturated solution of KCl. When membrane was not in used, kept in 0.01 M Th(NO<sub>3</sub>)<sub>4</sub> solutions to avoid damage by cracking.

Determination of thorium in Monazite ore and natural rock sample: Monazite normally contains 10–12 percent thorium dioxide (ThO<sub>2</sub>) and thus represents a major commercial source of thorium as well. 0.35 mg of monazite sand was dissolved in 25 mL of 55 % HNO<sub>3</sub> and solution was heated until the fumes were observed. 6 mL of water was added to the solution after it had been cooled to room temperature and the solution was again heated until fumes were observed. The same treatment was repeated till the time to ensure complete dissolution of the sample and the pH of the resulting solution was adjusted about 2.5-8.0. Final solution was transferred into a 100 mL volumetric flask and diluted up to the mark with water. Finally 3 mL of this solution was diluted to 500 mL in a volumetric flask with water.

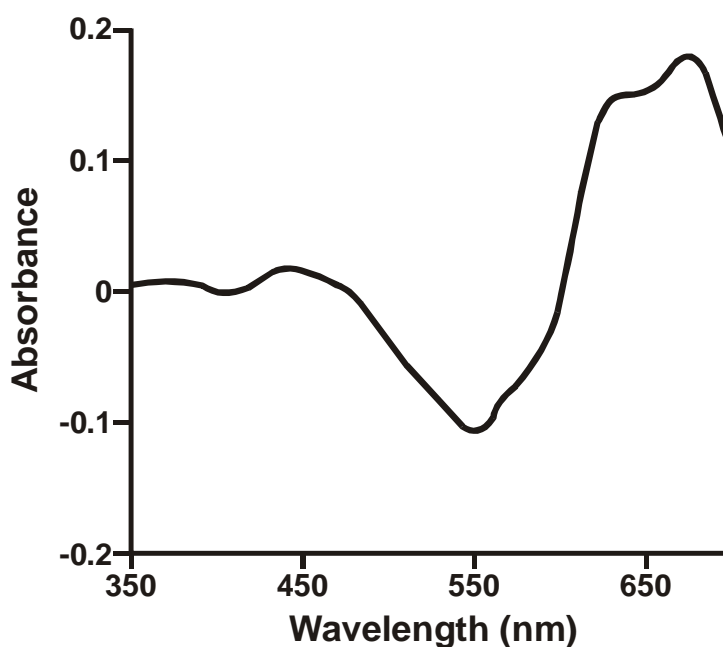
Determination of thorium in food samples: The food material was dried at 105 °C, ground in agate, and homogenized. Samples (10 g) were weighed in evaporating dishes and ashed at 500–550 °C in a muffle furnace. After that, the ash was dissolved with 10 mL of 0.1 M HNO<sub>3</sub>. Then it

was diluted. The process was repeated again 4-5 times and the resulting solution was transferred into a 100 mL volumetric flask and diluted up to the mark.

### 3. RESULT AND DISCUSSION

Presented research work involves the design and synthesis of *p*-tert-butyl-thiacalix[4]arene derivative alkyl group at phenolic position based receptor which shows extremely selectivity for Th(IV) metal. The size of the thiacalixarene cavity could be defined by the distances between the adjacent sulfur atoms. Various modifications of the parent calixarenes are also available both at the phenolic hydroxy groups and at the *p*-positions. Although replacement of the methylene units by hetero atom linkages such as -S-, would provide the calixarene analogues of quite interest because of the varied cavity sizes and the additional binding sites provided by the hetero atoms, such modifications have so far been quite difficult to carry out in substantial quantities [11,12]. The investigational results, which to confirm the response ability of the ion-selective electrodes to the activity changes due to the concentration change of the analyte ion, are summarized below.

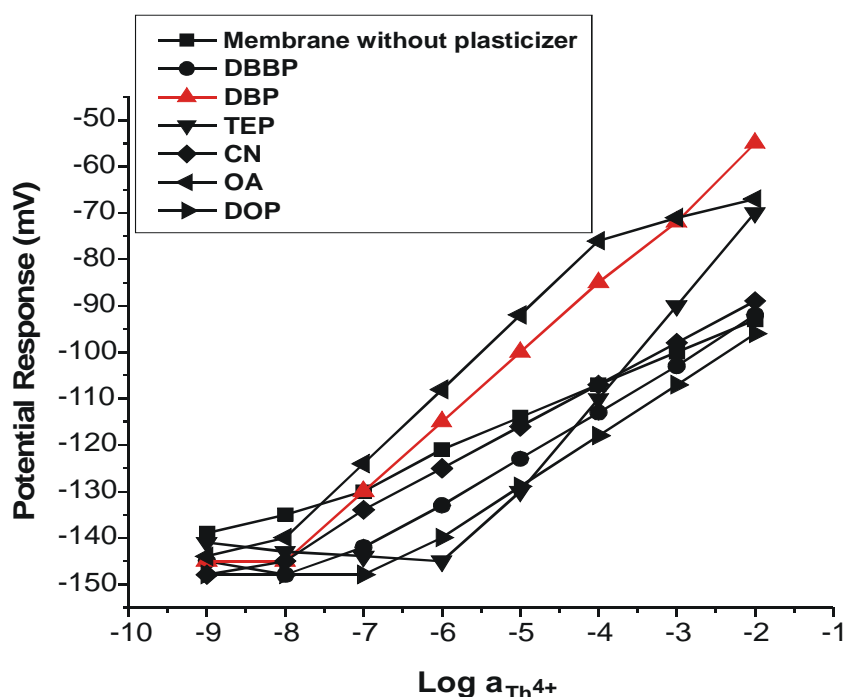
The absorption spectra of the Th(IV)-*p*-tert-butylcalix[4]arene derivative were taken under the experimental conditions. The Th(IV)-*p*-tert-butylcalix[4]arene derivative gives an absorption peak at 670 nm (Fig. 1). The absorption peak of 670 nm was chosen as the determination wavelength.



**Fig. 1.** Absorption spectra of the complex against the Th<sup>4+</sup> were measured by Lambda 35 UV/Vis Spectrophotometer

### 3.1. Membrane optimization

To monitor the effect of solvent mediator on the PVC membrane electrode, different plasticizers were used in the construction of the membrane electrode. The results are shown in Table 1 and Fig. 2. Membrane without plasticizer worked in the linear concentration range of  $1 \times 10^{-6}$ - $1 \times 10^{-1}$  M with Nernstian slope of  $10.5 \pm 0.5$  mV/decade and such values indicate the fact that plasticizer plays the significant role in membrane characterization and result improvement. And the plasticizers DBBP, DBP, TEP, 1-CN, OA, DOP were successfully tested for calibration slope, working concentration range, pH range, response time, selectivity coefficient for  $\text{Th}^{4+}$ . The membrane plasticized with DBBP showed narrow working concentration range as  $3.2 \times 10^{-7}$ - $1 \times 10^{-1}$  M with Nernstian slope of  $10.0 \pm 0.5$  mV/decade. Result obtained with plasticizers TEP, 1-CN, OA, DOP were also improper. The membrane having DBP as plasticizer exhibited best results (electrode no. 3). This sensor gave a Nernstian response (slope  $14.90 \pm 0.6$  mV/decade of activity) in the concentration range  $8.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M of  $\text{Th}^{4+}$  and a response time as fast as 7s. Therefore electrode no.3 with the optimum composition DBP:PVC:Ionophore:NaTPB (57%:35%:6%:2%) was chosen for all further studies. Repeated monitoring of potentials (20 measurements) on the same portion of the sample with this electrode gave a standard deviation of  $\pm 1.0$  mV. The sensing behavior of the membranes did not change when the potentials were recorded from lower to higher concentrations or vice-versa.



**Fig. 2.** Variation of potential of PVC based membrane of (I) (no.1) without solvent mediator and (nos. 2,3,4,5,6 and 7) with solvent mediators DBBP, DBP, TEP, 1-CN, OA, DOP respectively with  $\text{Th}^{4+}$  concentration

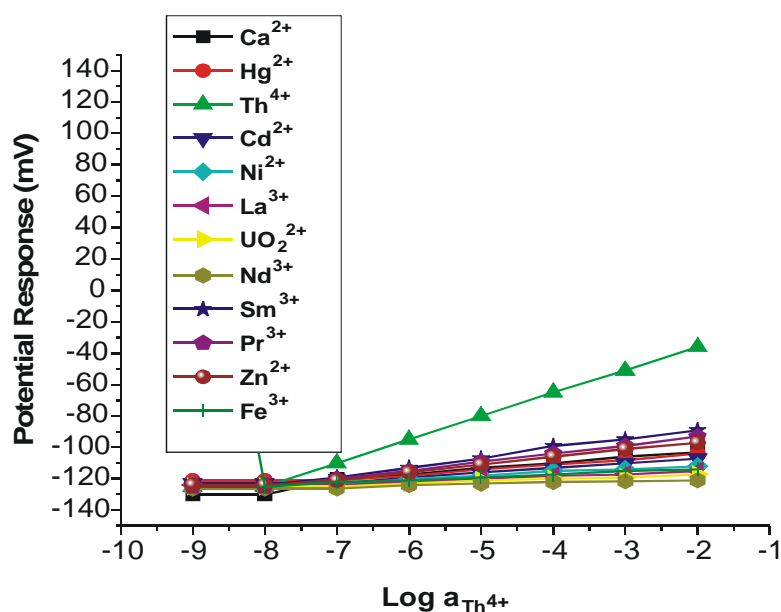
**Table 1.** Membrane optimization with different plasticizers i.e. membrane no.1 without plasticizers No.2,3,4,5,6,7 with DBBP,DBP,TEP,1-CN,OA,DOP and found that membrane electrode with plasticizers DBP (membrane-3) showed lowest concentration range among all

Membrane - No.	Composition of membrane (%)									Working Concentration Range (M)	Slope	Response Time (sec)
	DBBP (in %)	DBP (in %)	TEP (in %)	1-CN (in%)	OA (in %)	DOP (in %)	NaTPB (in %)	p-tert-butyl-thiacalix [4]arene derivative (in %)	PVC (in %)			
1							2	6	35	$1.2 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$7.00 \pm 0.1$	30
2	57						2	6	35	$3.2 \times 10^{-7}$ - $1.0 \times 10^{-1}$	$10.05 \pm 1.0$	15
3		57					2	6	35	$8.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	$14.90 \pm 0.6$	7
4			57				2	6	35	$1.6 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$22.03 \pm 0.1$	15
5				57			2	6	35	$3.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	$25.00 \pm 1.0$	25
6					57		2	6	35	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	$09.00 \pm 0.1$	28
7						57	2	6	35	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$	$11.05 \pm 0.1$	20

Calibration curve, measuring range and slope: The measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits (Fig. 3). The applicable measuring range of the proposed sensor is between  $8.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M with the near nernstian slope of  $14.9 \pm 0.6$  mV/decade of concentration. By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated.

Response and membrane stability period: The static response time required for the planned  $\text{Th}^{4+}$  sensor to reach a potential within  $\pm 1$  mV of the final equilibrium value was measured, after successive immersion in a series of  $\text{Th}^{4+}$  ion solution, each one having a 10-fold difference in concentration. Thus, the response time measured was 7 s (Fig. 4) over the entire concentration range. The potentials were sustained for at least 5 min, and the standard deviation of 10 identical measurements was  $\leq 0.5$  mV at several concentrations of  $\text{Th}^{4+}$  ions.

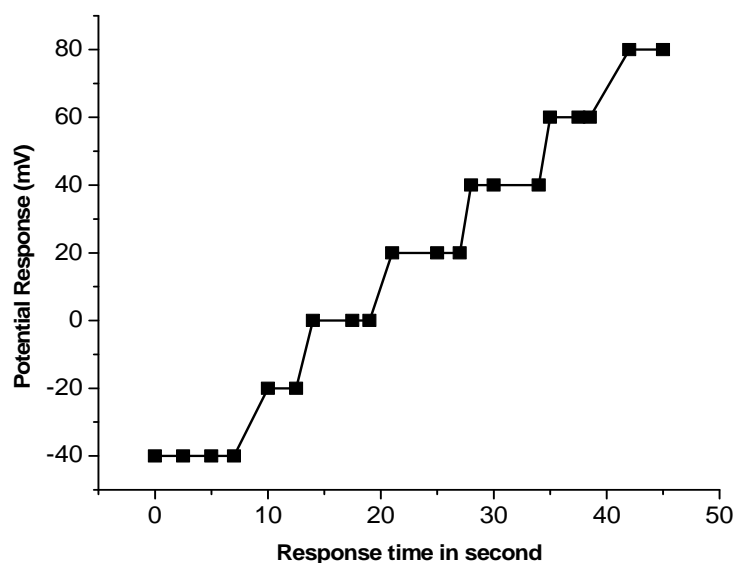
The loss of a plasticizer carrier or ionic sites from the polymeric film due to leaching into the sample solution is the primary reason for limited lifetimes of carrier-based sensors. Thus, the lifetime of a sensor based on ionophores in solvent polymeric membranes depends on the distribution coefficient of the ionophores and plasticizers between the aqueous and membrane phases [13]. The long term stability of the electrode was studied by periodically re-calibrating in standard solutions and collecting the response slope. The slope of the electrode response was reproducible over a period of at least 6 months. Thus, the proposed sensor could be used for 6 months with any considerable change in its response characteristics towards thorium cations.



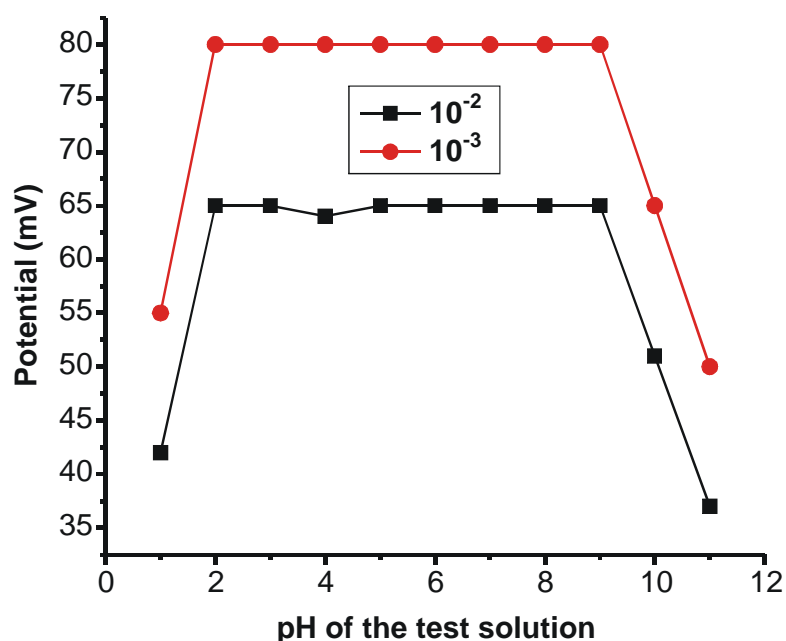
**Fig. 3.** Calibration curve versus potential for thorium cations using calix[4]arene derivative as an ionophore

pH and non-aqueous effect: Electrode response at different pH values was monitored by using two different concentrations of  $1.0 \times 10^{-2}$  M and  $1 \times 10^{-3}$  M respectively where the pH was adjusted with dilute  $HNO_3$  or hexamine solutions to achieve acidic and basic medium respectively. Response potential remain constant from pH of about 2.0-9.0 that is wider range as compared to data required with previously reported electrodes for  $Th^{4+}$  ions (Fig. 5). So our membrane electrode can work in both medium i.e. acidic medium as well as basic medium. Above and below this pH range, potential response changes considerably. It was found that the sensor assembly worked well in non-aqueous media having a 40% (v/v) alcoholic content without showing any appreciable change in the working concentration range or slope (Table 2).





**Fig. 4.** Dynamic response time curve versus potential response for  $\text{Th}^{4+}$ -selective ion-selective electrode



**Fig. 5.** Effect of pH versus potential response on  $\text{Th}^{4+}$  ions solution (a)  $\text{Th}^{4+}=1.0 \times 10^{-2}$  M, (b)  $\text{Th}^{4+}=1.0 \times 10^{-3}$  M for sensor no. 3

Selectivity: Selectivity is key parameter of any ion selective electrode. And it can be describe in terms of selectivity coefficient. We measured selectivity by match potential method [14]. In match potential method, the specific activity of the primary ion is added to a reference solution

and then potential is measured. Apart from that in a separate experiment interfering ions were gradually added to an identical reference solution until the measured potential matched that obtained before by adding the primary ions. By match potential method selectivity coefficient is given by the resulting primary ion to interfering ion activity ratio.

$$K_{Th^{4+}, B} = a_{Th^{4+}}/a_B$$

The resulting value obtained from MPM for thorium determination, are given in table and shows that the electrode do not face interference if these ions present in lesser amount (Table 3).

**Table 2.** Effect of non-aqueous solvents on the calibration curve and response time of proposed functionalized calix[4]arene derivative based PVC membrane electrode for Th<sup>4+</sup> ion

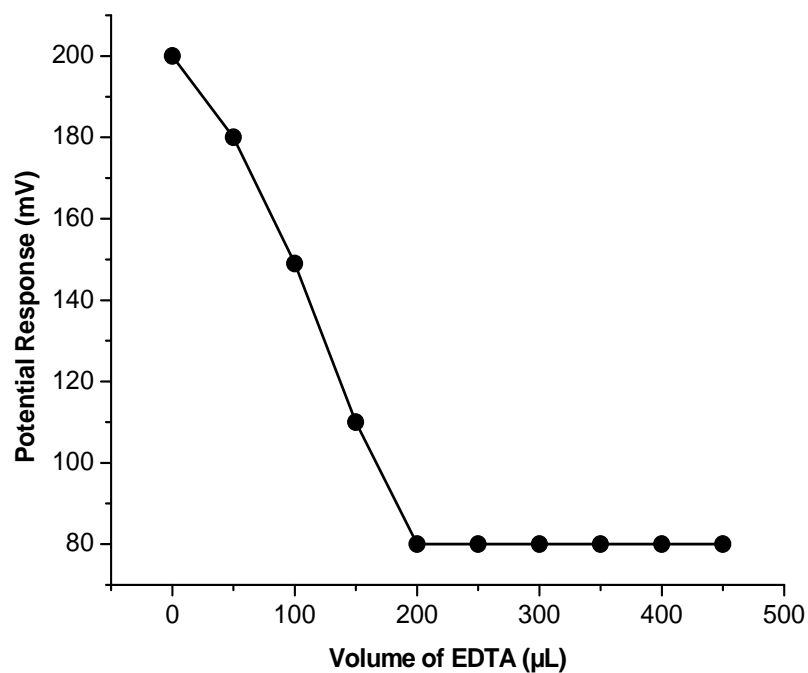
Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. range(M)	Response time (seconds)
0	14.90±0.6	8.0×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
<b>Methanol</b>			
10	14.05±1.0	7.9×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
20	13.00±1.0	7.7×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
30	12.40±1.0	7.2×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
40	12.05 ±1.0	7.1×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
<b>Ethanol</b>			
10	14.05±1.0	7.8×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
20	13.50±1.0	7.5×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
30	13.01±1.0	7.3×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
40	12.00±1.0	7.1×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
<b>Acetone</b>			
10	14.00±1.0	7.5×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
20	13.09±1.0	8.0×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
30	12.99±1.0	7.1×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
40	12.50±1.0	6.9×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	9
<b>Acetonitrile</b>			
10	14.50±1.0	8.0×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8
20	14.10±1.0	7.8×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
30	13.90±1.0	7.3×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	7
40	13.01±1.0	6.8×10 <sup>-8</sup> -1.0×10 <sup>-1</sup>	8

**Table 3.** Calculation of selectivity coefficient by Match potential method for a number of metal ions

Interfering ion (M <sup>n+</sup> )	Selectivity Coefficient, $K_{Th^{4+}, M^{n+}}^{POT}$
	Match Potential Method
K <sup>+</sup>	1.2×10 <sup>-5</sup>
Ca <sup>2+</sup>	1.6×10 <sup>-5</sup>
Mg <sup>2+</sup>	2.5×10 <sup>-4</sup>
Al <sup>3+</sup>	1.4×10 <sup>-6</sup>
Cd <sup>2+</sup>	3.3×10 <sup>-5</sup>
Hg <sup>2+</sup>	2.5×10 <sup>-5</sup>
Ni <sup>2+</sup>	4.9×10 <sup>-4</sup>
Fe <sup>3+</sup>	5.2×10 <sup>-5</sup>
Zn <sup>2+</sup>	3.5×10 <sup>-5</sup>
La <sup>3+</sup>	1.6×10 <sup>-6</sup>
Ce <sup>3+</sup>	4.2×10 <sup>-6</sup>
Nd <sup>3+</sup>	2.3×10 <sup>-6</sup>
Sm <sup>3+</sup>	3.5×10 <sup>-6</sup>
Pr <sup>3+</sup>	2.8×10 <sup>-6</sup>
UO <sub>2</sub> <sup>2+</sup>	2.0×10 <sup>-6</sup>

Potentiometric titration: This calixarene based sensor was successfully applied as an indicator electrode in the potentiometric titration of Th<sup>4+</sup> ions with EDTA. 50 mL (1.0×10<sup>-3</sup> M) solution of Th<sup>4+</sup> was titrated against 1.0×10<sup>-2</sup> M EDTA at pH 6.5 (Fig. 6). The plot does not have standard sigmoid shape. However, the sharp break point corresponds to the stoichiometry of Th<sup>4+</sup>- EDTA complex.

Determination of thorium in different sample: This electrode was successfully applied for the thorium determination in sedimentary rock and monazite ore. The result came from membrane ion selective electrode, were cross-checked by atomic absorption spectrophotometry (AAS) (Table 4).



**Fig. 6.** Potentiometric titration curve of 50 ml of  $10^{-3}$  M  $\text{Th}^{4+}$  solution  $\text{Th}(\text{NO}_3)_3$  with  $1.0 \times 10^{-2}$  M of EDTA using the membrane electrode as an indicator electrode

**Table 4.** Determination of thorium in different sample such as monazite ore, sedimentary rock sample, Potato, Milk, Rice

Samples	AAS ( $\mu\text{g/L}$ )	Proposed Methods ( $\mu\text{g/L}$ )
Monazite Ore	$2.04 \pm 0.5$	$2.02 \pm 0.9$
Sedimentary rock sample	$3.19 \pm 0.5$	$3.15 \pm 0.8$
Potato	$0.599 \pm 0.007$	$0.599 \pm 0.001$
Milk	$6.485 \pm 0.002$	$6.483 \pm 0.008$
Rice	$1.595 \pm 0.003$	$1.592 \pm 0.009$

**Table 5.** Comparison of the reported thorium selective electrodes with proposed electrode assembly

Sensor No.	Ionophore name	Working Conc. Range (M)	Slope (mV/decade pH of activity)	pH range	Response Time (s)	Life time	Selectivity	Reference
1	Thorium 8-	$5.0 \times 10^{-6} - 1 \times 10^{-1}$	$15.5 \pm 0.5$	3.0-5.0	30	2 months	-	5
2	Tin(IV) tungstoselenate pyridine	$8.0 \times 10^{-6} - 1.0 \times 10^{-1}$	$14.2 \pm 1.0$	2.5-9.0	15	-	Alkali, alkaline and transition	6
3	5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis(diphenyl	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	$15.5 \pm 0.5$	4.0-2.3	15	6 months	$\text{Li}^{2+}$ , $\text{Na}^{+}$ , $\text{K}^{+}$ , $\text{Ag}^{+}$ , $\text{NH}_4^{+}$ , $\text{Sr}^{2+}$ , $\text{Mn}^{2+}$ ,	7
4	2,3,7,8-tetraphenyl-1,4,6,9-tetraaza-	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	$14.2 \pm 0.3$	3.5-9.5	10	5 months	Over variety of metal ions	8
6	<i>p</i> -tert-butyl-thiacalix[4]arene derivative	$8.0 \times 10^{-8} - 1.0 \times 10^{-1}$	$14.9 \pm 0.6$	2.0-9.0	5	6 months	Over a large number of	This work

#### 4. CONCLUSION

The presented research favored that this calixarene derivative function as an excellent ionophore for  $\text{Th}^{4+}$  selective membrane sensor. The proposed sensor is superior in terms of linear range, detection limit, selectivity coefficients, and response time to the previously reported ones (Table 5). The sensor no. 3 having membrane with composition DBP:PVC:Ionophore:NaTPB in ratio of 57%:35%:6%:2% (w/w), was found to perform best. Membrane electrode has good potentiometric figures of merit for the determination of thorium ions, including high sensitivity, low detection limit ( $8.0 \times 10^{-8}$  M), fast response time (7s), good Nernstian slope (14.9 mV/decade) and wide linear range ( $8.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M) with respect to  $\text{Th}^{4+}$  ion concentration.

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